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# FABRICATION AND CHARACTERIZATION OF MASTERBATCHES MADE FROM POLY(VINYL CHLORIDE) AND MODIFIED FLY ASH

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## Abstract

Masterbatches made from plasticized poly(vinyl chloride) (PVC compound) and modified fly ash by stearic acid (MFA) or unmodified fly ash (FA) were fabricated by extrusion method using a twin-screw extruder. The relative melt viscosity, tensile properties, dielectric properties and flame retardance of the masterbatches were characterized by using Haake Rheomix 9000 (Germany), tensile measurement (Zwick I V2.5, Germany), dielectric measurement (Aglient instruments model E4980A, USA) and vertical burning test (as per UL 94, USA), respectively. The results indicate that FA increase the viscosity of PVC compound, while MFA significantly reduces the viscosity of PVC compound. It means that modification of FA by stearic acid is an advantage way for improving the processability of the PVC- filler masterbatches. Young's modulus of PVC/FA and PVC/MFA masterbatches increases as increasing filler content. However, tensile strength and elongation at break of the masterbatches strongly reduce due to high filler content. Fortunately, there is a slightly enhancement effect on the tensile strength and elongation at break when using MFA instead of original FA. The density of the masterbathches is increased as function of filler content. It is interesting to know that the dielectric constant of PVC/FA and PVC/MFA masterbatches is propotional to the FA and MFA content. The flame retardance of PVC/FA and PVC/MFA masterbatches is classified as V-0 and V-1 rating in UL VB 94 test.

**Keywords.** Modified fly ash, masterbatch, PVC, processability, dielectric, flame retardance.

## 1. INTRODUCTION

Fly ash (FA) is the waste product produced from the combustion of pulverized coal in thermoelectric power plants. In Vietnam, millions of tons of coal ash are produced annually from these power plants, this amount of ash will cause a great impact on the environment [1]. Fortunately, coal ash from two power plants in Pha Lai province has been collected and afterward FA is selected by using the sink/flotation technology. This kind of FA is mainly used as additive for making light weight concretes, unfired bricks, road construction material [1, 2]. The utilization of FA will not only reduce the environment concerns but also bring economic benefits. It is known that FA consists mostly of $SiO_2$, $Al_2O_3$, $Fe_2O_3$ and some other oxides with their low contents [2, 3]. Therefore, FA has been also used as an alternative filler for polymers, such as polyethylene [4], polypropylene [5], poly(vinyl chloride) [5], epoxy resins [6], rubbers [7], polyphenylene oxide [8], etc. However, the major problems in fly ash filled polymer composites are caused by the weak interfacial adhesion and the poor dispersion of this filler in the polymer matrix [9]. Surface modification of FA is an effective way to solve these problems by enhancing interfacial interactions between the polymer and inorganic fillers as well as improving the organic affinity for FA. It was reported in the literature that the dispersion of modified fly ash and the mechanical, rheological, thermal properties and moisture absorption of modified FA-filled polymer composites are improved [10]. In our previous studies, FA was also modified by some coupling agents or fatty acids [11-13]. The results have shown that modified FA (MFA) can disperse into polyethylene (PE) or polyvinyl chloride (PVC) more regularly than unmodified FA. Melt processing ability, tensile strength and elongation at break of MFA composites are also improved. Despite the reduction in electrical resistivity, PE/MFA, PVC/MFA composites are still good electrical insulation materials.

In plastic industry, production of masterbatches with large amount of fillers is the most effective way to reduce the cost and improve processing of plastic products. In our previous studies, the FA or MFA is used at low content (up to 20 wt.%). Therefore, the aim of this study is to produce the masterbatches made from PVC and MFA with their higher content. With potential of PVC/FA composites for insulation application, the mechanical, electrical properties and flame retardance of the composites have been thoroughly examined. The effect of MFA content on these properties of the composites will be also discussed.

## 2. EXPERIMENTAL

### 2.1. Materials

Fly ash silo (FA) was provided by Pha Lai Thermoelectric Power Plant (Vietnam) after sink/flotation separation processes. The average particle size of selected FA is about 5 µm, 84wt.% passing the 325-mesh sieve (45 µm), total weight of $SiO_2$, $Al_2O_3$ and $Fe_2O_3$ more than 86 % and moisture content less than 0.3 %.

PVC (SG-660 type) with K index of 65-67 was supplied by TPC Vina Plastic & Chemical Corp., Dong Nai, Vietnam. Dioctyl phthalate (DOP), stearic acid are commercial products made in Korea. Stabilizer with trade name of Irgastab 17M (dibutyl-tin diisooctylthioglycolate) was a product of Ciba Geigy Ltd. (Switzerland). Cadmium, barium and zinc stearates (Cd-, Ba-, Zn-Stearate) were supplied by Institute for Technology of Radioactive and Rare Elements (ITRRE, Vietnam). Epoxidized soybean oil (ESO) with epoxy group content of 15.2 wt.% was obtained from Malaysia.

### 2.2. Modification of FA by stearic acid

FA was first dried at 110 °C for 4 hours in a circulating hot air oven. By using solid-state modification (not using any solvent), FA was modified by stearic acid (with 3 wt.% compared to FA weight) in SHR 100A high speed mixer (China) at 70°C, 600 rpm for 2 hours. The mixture was then milled and stored in PE bags. Modified FA was obtained and denoted as MFA.

### 2.3. Fabrication of FA-filled PVC masterbatches

PVC powder and additives: DOP, Irgastab 17M, ESO, Cd-, Ba-, Zn-Stearates (all additives are compared to PVC powder weight) were mixed with their content 100:30:2:1:1:1:1 in SHR 100A high speed mixer at 105 °C for 10 minutes. Then, the mixture was put into circulating hot air oven at 100 °C for 2 hours to give dry and suitable powder compound. The PVC compound and FA or MFA with different content were mixed in SHR 100A high speed mixer for 5 minutes at room temperature. Masterbatches based on these mixtures were fabricated by twin-screw extruder (Shanghai, China). The temperature on 4 zones of cylinder were 170, 175, 180, 190 $^oC$ (from feeding zone to forming zone/die zone). The masterbatches containing 30, 35, 40, 45, 50 wt.% of unmodified FA or MFA, were coded as MB30U, MB35U, MB40U, MB45U, MB50U or MB30S, MB35S, MB40S, MB45S, MB50S, respectively. The masterbatch made by PVC compound without FA or MFA was coded as PVC30.

For preparation of testing samples, masterbatches in granule form were melt blended at 180 °C and 50 rpm rotor speed in a Haake Intermixer (Germany) for 4 minutes. Finally, melt mixtures were quickly taken out and molded by a hot pressured instrument (Toyoseiky, Japan) to form flat samples for testing afterwards.

### 2.4. Characterizations and methods

The torque diagrams in melt mixing state of PVC filled FA or MFA composites were recorded at 180 °C by Polylab 3.1 software connected to the Haake intermixer. The relative melt viscosity is evaluated by the mixing torque at steady melt-state for each sample.

Mechanical properties (Young's modulus, tensile strength, elongation at break) of the composites were measured by using a Zwick tensile tester (Germany) at room temperature with a crosshead speed of 100 mm/min, according to ASTM D638. The values were averaged from 5 specimens for each series of masterbatch.

Relative dielectric permeability (dielectric constant) and dielectric loss of the composites were tested by Agilent instruments model E4980A with the 16451B test fixture for solid materials, according to ASTM D150.

Vertical burning test of the composites was conducted on a flammability-testing instrument (Vietnam) according to the UL-94 HB (USA). The test was carried out at 25 $^oC$ and relative humidity of 60 %. The specimens were prepared in rectangular with dimensions of 127 mm × 12.7 mm × 3 mm. A series set of 5 specimens was prepared for each PVC filled FA masterbatch.

All above experimental measurements were carried out at Institute for Tropical Technology, Vietnam Academy of Science and Technology.

## 3. RESULTS AND DISCUSSION

### 3.1. Relative melt viscosity

Figures 1 and 2 display the mixing torques as function of mixing time of PVC/FA and PVC/MFA masterbatches containing different FA, MFA contents, respectively. It can be seen from these figures that the steady-melt state of PVC masterbatches can be taken from 3rd to 4th minute of mixing, which are plotted in the small windows inside the figures.

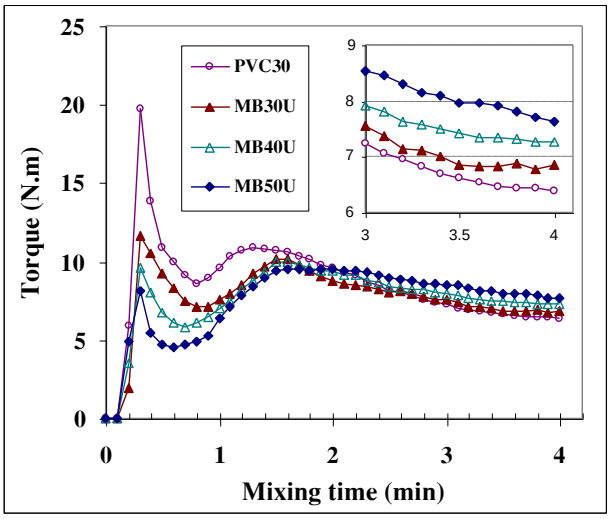


*Figure 1:* Torque of PVC/FA masterbatches as function of mixing time

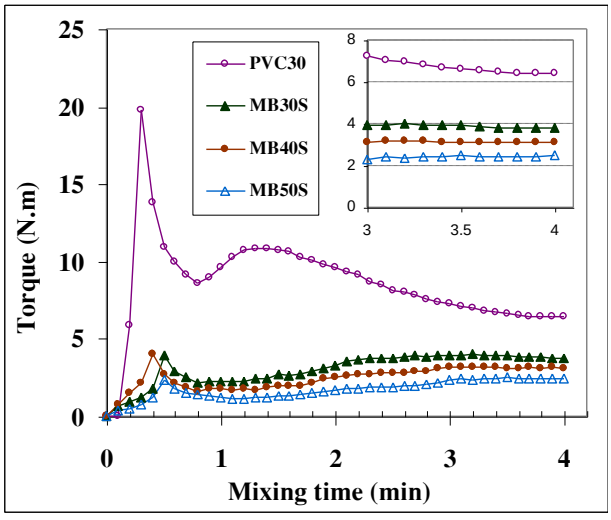


*Figure 2:* Torque of PVC/MFA masterbatches as function of mixing time

As demonstrated in the previous studies [11], the steady-melt torque of the polymer composites is a measure of melt viscosity of the composites and called the relative and melt viscosity. Therefore, the results in figure 1 indicate that the relative melt viscosity of PVC/FA masterbatches (MB30U, MB40U, MB50U) is higher than that of PVC compound (PVC30) and increases with increasing unmodified FA content. In contrast, the results in Figure 2 indicate that when using MFA, the relative melt viscosity of PVC compound is decreased considerably. This is an expected result because the modification of FA has improved the processing ability (processability) for the masterbatches.

### 3.2. Tensile properties and density

Tables 1 and 2 represent tensile properties of the PVC filled FA and MFA masterbatches, respectively. It is clear that the Young's modulus (E) of PVC compound increases with increasing FA or MFA content (varied from 30 to 50 wt.%). This can be explained by that FA fillers are rigid particles, when dispersed into PVC compound, they decrease the mobility of the PVC macromolecule chains when an external force is applied in Young's modulus measurement. However, E modulus of PVC/MFA masterbatch samples is lower than that of PVC/FA samples at the same content. The season for that may from the presence of stearic acid that is used as an agent for improving dispersion of FA and the processability of the masterbatches.

*Table 1:* Tensile properties and density of PVC/FA masterbatches

| Sample code | E (MPa) | $\sigma_b$ (MPa) | $\varepsilon_b$ (%) | Density (g/cm³) |
|---|---|---|---|---|
| PVC30 | 46±2 | 23.7±0.4 | 314±9 | 1.273 |
| MB30U | 75±5 | 14.0±0.4 | 171±7 | 1.451 |
| MB35U | 78±6 | 13.2±0.1 | 162±2 | 1.478 |
| MB40U | 86±9 | 11.3±0.2 | 163±2 | 1.509 |
| MB45U | 90±6 | 10.2±0.1 | 149±2 | 1.548 |
| MB50U | 94±9 | 8.3±0.2 | 130±2 | 1.582 |

Tables 1 and 2 also show that tensile strength ($\sigma_b$) and elongation at break ($\varepsilon_b$) of PVC/FA and PVC/MFA masterbatches strongly decrease when increasing FA content from 30 to 50 wt.%. That is mainly due to high content of filler causing the agglomeration of FA. Fortunately, the $\sigma_b$ and $\varepsilon_b$ of PVC/MFA masterbatches are slightly higher than those of PVC/FA masterbatches at the same content.

It means that the modification of FA has improved dispersion of MFA particles and reduced their agglomeration into the PVC matrix. It is also seen that the density of PVC/FA and PVC/MFA samples increases as function of filler content. Due to better filler dispersion, the density of PVC/MFA is slightly higher than that of PVC/FA samples at the same content.

*Table 2:* Tensile properties and density of PVC/MFA masterbatches

| Sample code | E (MPa) | $\sigma_b$ (MPa) | $\varepsilon_b$ (%) | Density (g/cm³) |
|---|---|---|---|---|
| PVC30 | 46±2 | 23.7±0.4 | 314±9 | 1.273 |
| MB30S | 47±4 | 14.4±0.5 | 194±5 | 1.460 |
| MB35S | 52±8 | 13.6±0.2 | 186±3 | 1.486 |
| MB40S | 61±5 | 11.9±0.1 | 175±2 | 1.520 |
| MB45S | 69±9 | 10.8±0.1 | 166±2 | 1.558 |
| MB50S | 77±4 | 9.0±0.1 | 147±4 | 1.593 |

### 3.3. Dielectric properties

Figures 3 and 4 perform the variation of dielectric constant of PVC/FA and PVC/MFA masterbatches as function of frequency, respectively. It can be seen that the increase in frequency decreases the magnitude of dielectric constant; and the increase in FA content increases the dielectric constant of PVC filled FA masterbatches. This is simply explained by that at low frequencies, the dipoles in the materials can follow the force generated by applied alternative field, but when frequency increases, it is more difficult for the dipoles to follow the alternative field. It means that at lower frequencies, the material becomes more polar, and at higher frequency the material seems less polar. The dielectric constant of FA (with values about 5-10 at 1000 Hz, depending on water, carbon contents and other constituents [14]) is much larger than that of plasticized PVC (with value of 3.76 at 1000Hz). Therefore, FA increases the dielectric constant of PVC compound. At every frequency, it is interesting to see that dielectric constant of PVC/FA and PVC/MFA masterbatches is proportional to the FA content.

For more detail information about the effect of FA content, Figure 5 displays the dielectric constant of the PVC/FA ($\varepsilon_{MB\text{-}FA}$) and PVC/MFA ($\varepsilon_{MB\text{-}MFA}$) masterbatches at 1 kHz as function of FA content ($C_{FA}$), and the linear equations are displayed inside. From these equations, the dielectric constant of FA or MFA can be evaluated by assuming that FA or MFA contents ($C_{FA}$ or $C_{MFA}$) are 100 (wt.%), and their calculated values are of 5.58 and 5.32, respectively. The results indicate that the modification of FA by stearic acid reduces the dielectric constant of FA.

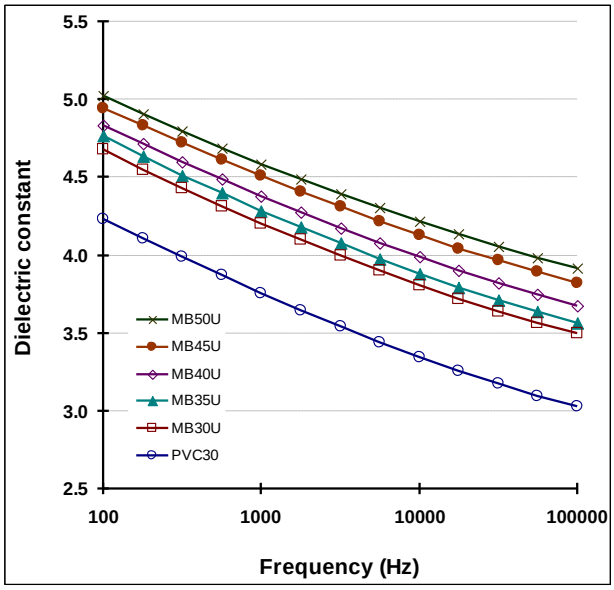


*Figure 3:* Dielectric constant of PVC/FA masterbatches as function of frequency

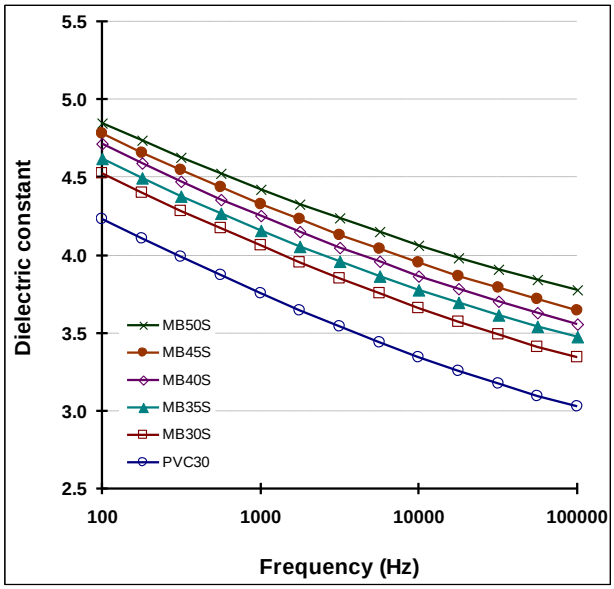


*Figure 4:* Dielectric constant of PVC/MFA masterbatches as function of frequency

Table 3 shows the dielectric loss tangent measured at 1 kHz of PVC/FA and PVC/MFA masterbatches. For electric insulation materials, the requirement for this parameter is as small as possible. In the selection of FA, the residue carbon was mostly removed therefore, the selected FA is suitable filler for plastic as insulation material. The

results in Table 3 show that both FA and MFA can reduce the dielectric loss of the PVC compound with no remarkable difference and the values are in order of $10^{-2}$.

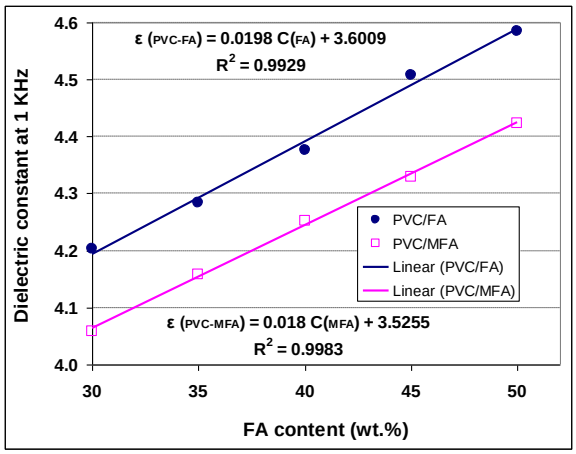


*Figure 5:* Dielectric constant at 1 kHz of masterbatches as function of FA (or MFA) content

*Table 3:* Dielectric loss tangent at 1 kHz of PVC compound as function of FA content

| FA content (wt.%) | PVC/FA | PVC/MFA |
|---|---|---|
| 0 | 0.081 | 0.081 |
| 30 | 0.076 | 0.073 |
| 35 | 0.071 | 0.067 |
| 40 | 0.066 | 0.068 |
| 45 | 0.059 | 0.064 |
| 50 | 0.056 | 0.062 |

### 3.4. Flame retardance

Table 4 presents the total after flame times ($t_1$+$t_2$) of 5 specimens and classification of vertical burning rating for the PVC filled FA masterbatches. It was observed in the burning measurement that all specimens were able to catch fire after two steps of ignition for 10 seconds (after that flame time was measured). However, the specimens were self-extinguished caused by hydrochloride gas generated, therefore the after flame time was short.

The results in table 4 indicate that the flame retardance of PVC compound is improved when using FA content less than 40 %. This effect is not occurred with MFA filled PVC masterbatches. The reason may be that stearic acid used for modification of FA is flammable while original FA is inflammable. However, when using FA or MFA loading at lower 45 wt.%, the VB rating of the masterbatches is classified as V0, the highest class of flame retardance in UL VB 94 test. When using 50 wt.% of FA or MFA, the masterbatches are classified as V1 rating. That means, the after flame time is longer due to the strong agglomeration of FA fillers in PVC matrix.

*Table 4:* Total after flame time ($t_1$ and $t_2$) of set 5 specimens for PVC/FA and PVC/MFA masterbatches

| FA content (wt.%) | PVC/FA | | PVC/MFA | |
|---|---|---|---|---|
| | ∑ ($t_1$+$t_2$) (s) | VB class | ∑ ($t_1$+$t_2$) (s) | VB class |
| 0 | 17.5 | V0 | | |
| 30 | 12.5 | V0 | 19.5 | V0 |
| 35 | 13.0 | V0 | 19.5 | V0 |
| 40 | 14.0 | V0 | 27.5 | V0 |
| 45 | 18.5 | V0 | 30.0 | V0 |
| 50 | 51.0 | V1 | 55.0 | V1 |

## 4. CONCLUSION

The melt viscosity of PVC/FA and PVC/MFA masterbatches is increased as increasing FA content, while MFA reduces melt viscosity of PVC. Both FA and MFA increase Young's modulus of PVC compound. Tensile strength and elongation at break of the PVC/FA and PVC/MFA masterbatches strongly reduce with rising FA and MFA content. There is an enhancement effect on the tensile strength and elongation at break when using MFA instead of FA. The density of the masterbatches is proportional to FA and MFA loading. At the same frequency, dielectric constant of the masterbatches increases with rising FA and MFA content. The dielectric loss values of the masterbatches and PVC compound are in order of $10^{-2}$. The flame retardance of PVC/FA and PVC/MFA masterbatches is classified as V-0 and V-1 rating in UL VB 94 test.

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